Charge and energy transport in films of touching nanocrystals

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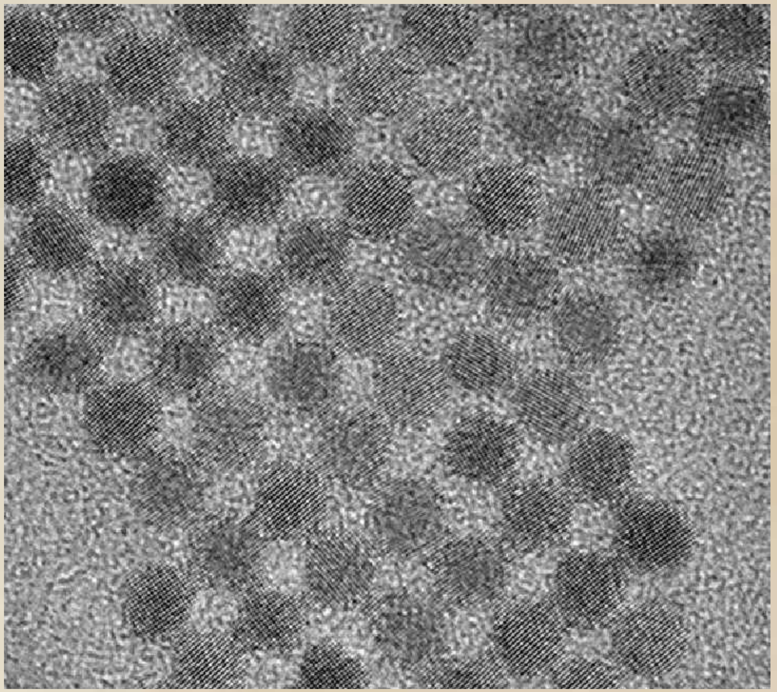
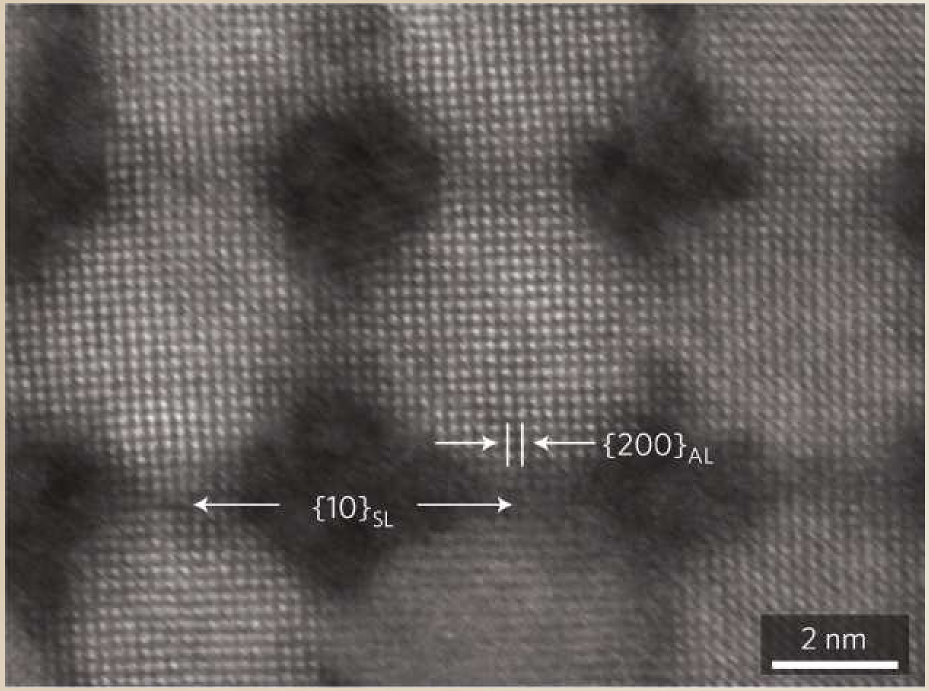
Touching nanocrystals

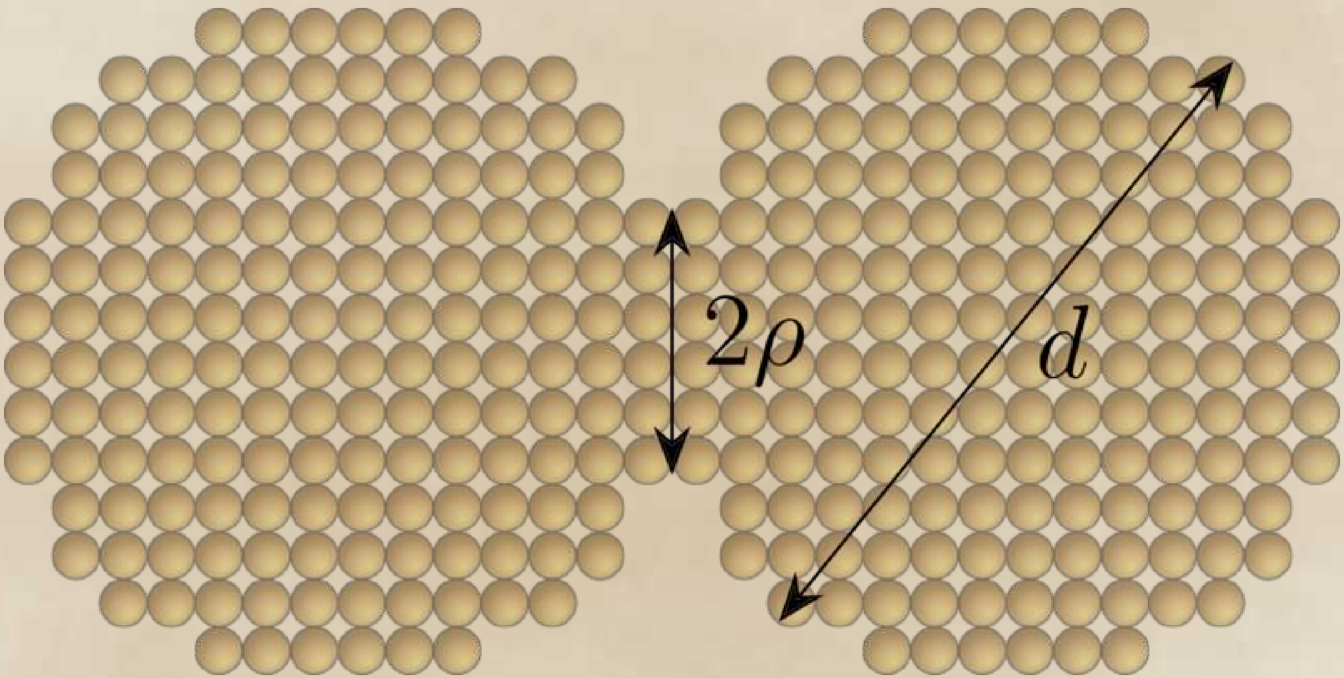


Houtepen group, ACS Nano (2014)



Hanrath group, Nature Materials (2016)

Touching nanocrystals



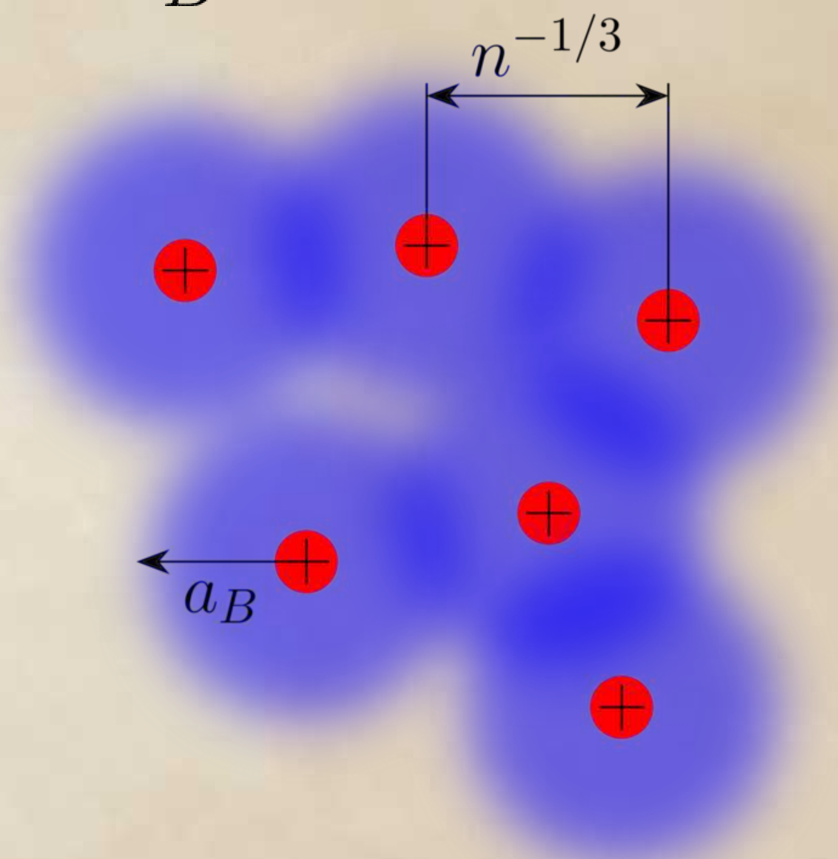
How many electrons make a semiconductor nanocrystal film metallic?

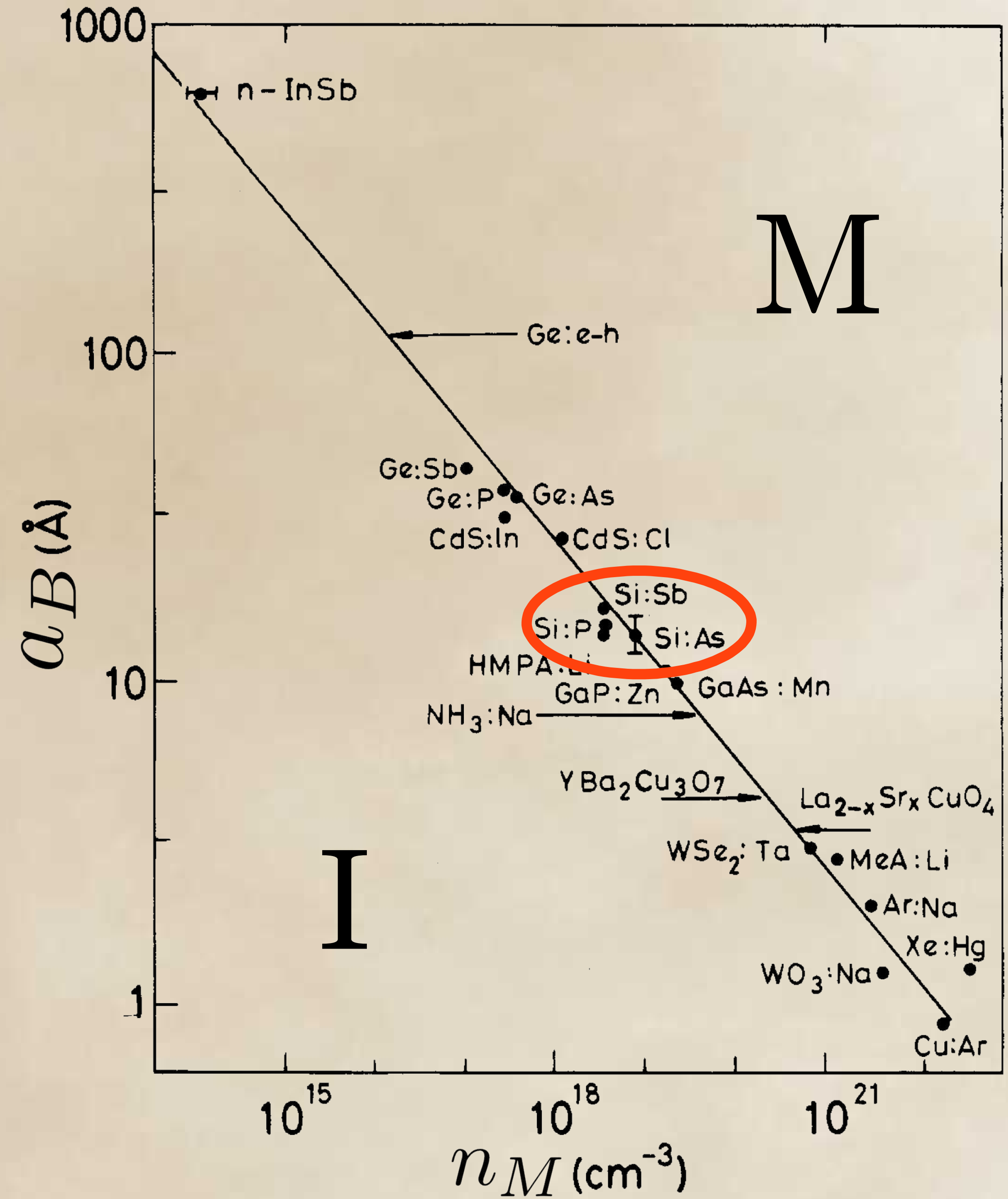
How excitons hop between semiconductor nanocrystals?

How many electrons make bulk semiconductor metallic?

Mott criterion

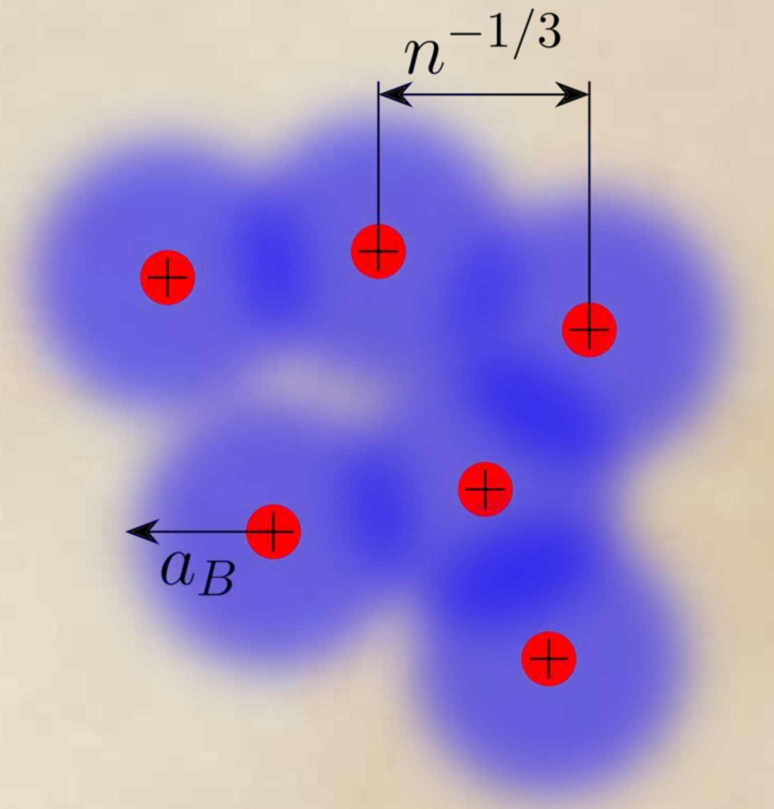
$$n_M a_B^3 \simeq 0.02$$



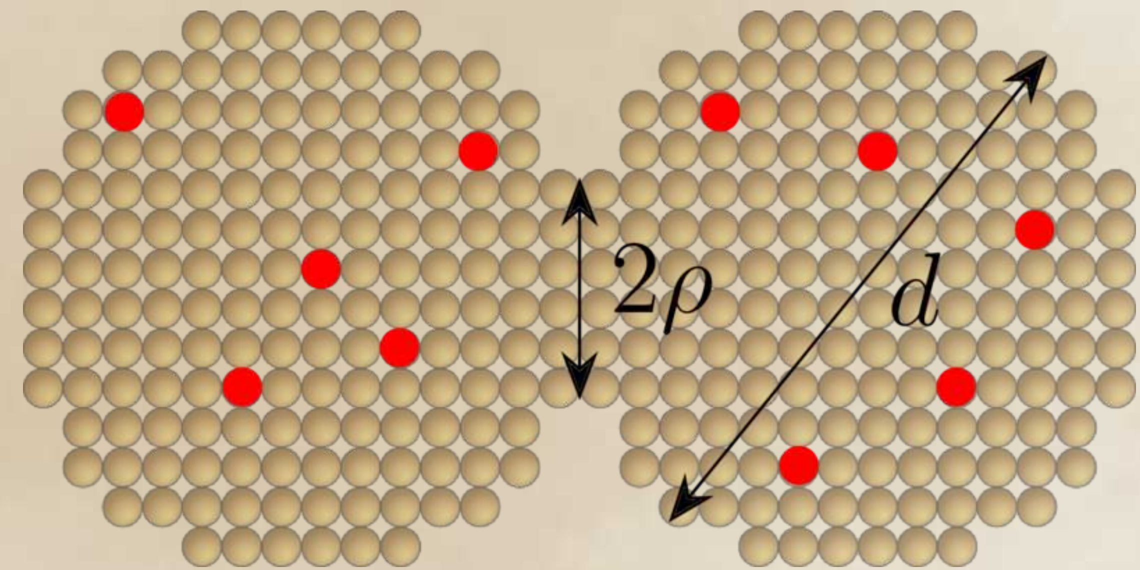


Metal insulator transition

In bulk Si



In touching Si "metallic" nanocrystals



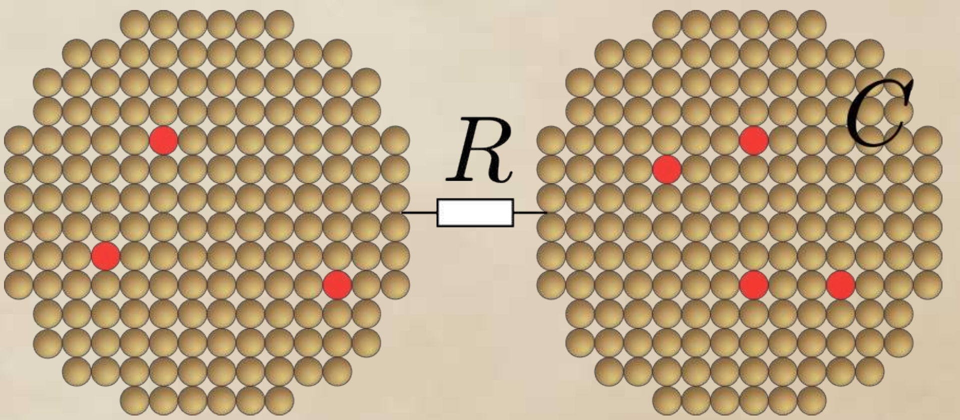
$$n_M a_B^3 \simeq 0.02$$

$$n \simeq 3 \times 10^{18}\ \mathrm{cm}^{-3}$$

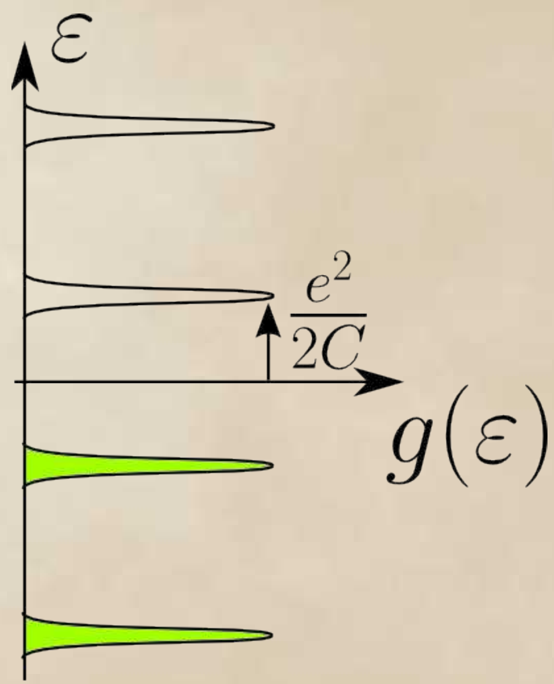
$$n_c \rho^3 \simeq 0.3$$

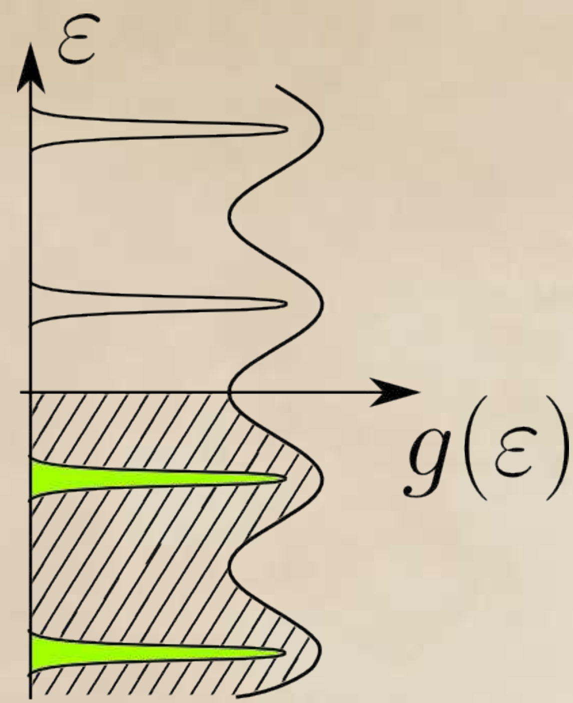
$$n_c \simeq 5 \times 10^{20}\ \mathrm{cm}^{-3}$$

Metallic connection



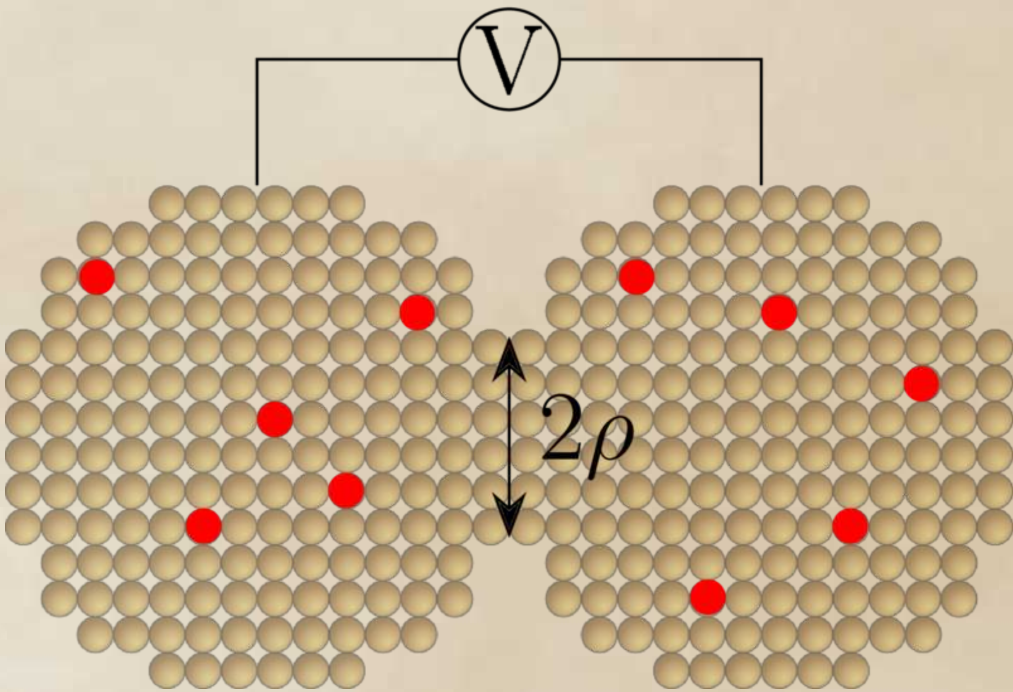
$$G = \frac{1}{R} > \frac{e^2}{\hbar}$$

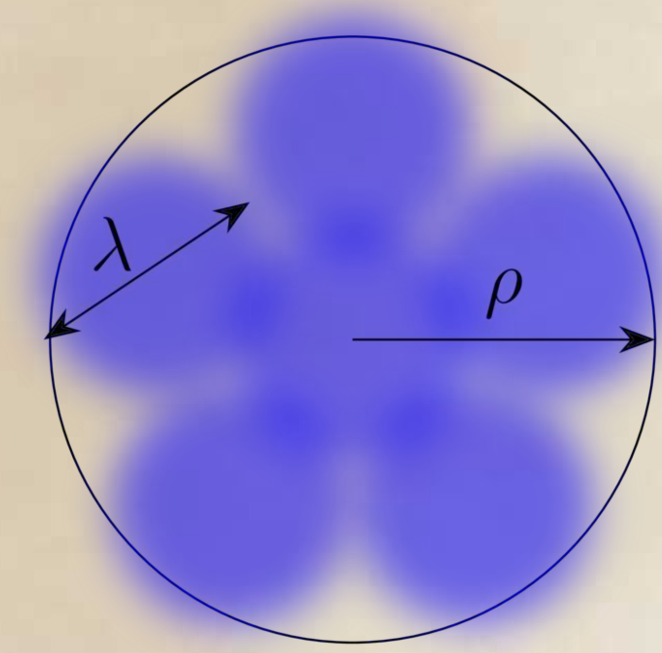




$$\frac{\hbar}{RC} > \frac{e^2}{C}$$

Sharvin conductance





$$\lambda \simeq n^{-1/3}$$

$$G = \frac{e^2}{\hbar}\left(\frac{\rho}{\lambda}\right)^2$$

Sharvin (1965)

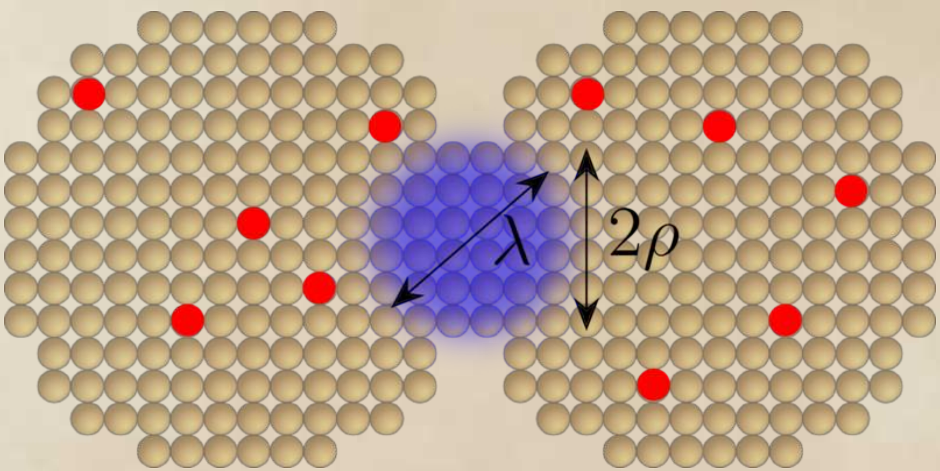
Approaching metal-insulator transition from the metallic side

$$G_c = \frac{e^2}{\hbar}$$

$$G = \frac{e^2}{\hbar}\left(\frac{\rho}{\lambda}\right)^2$$

$$\rho \simeq \lambda \simeq n_c^{-1/3}$$

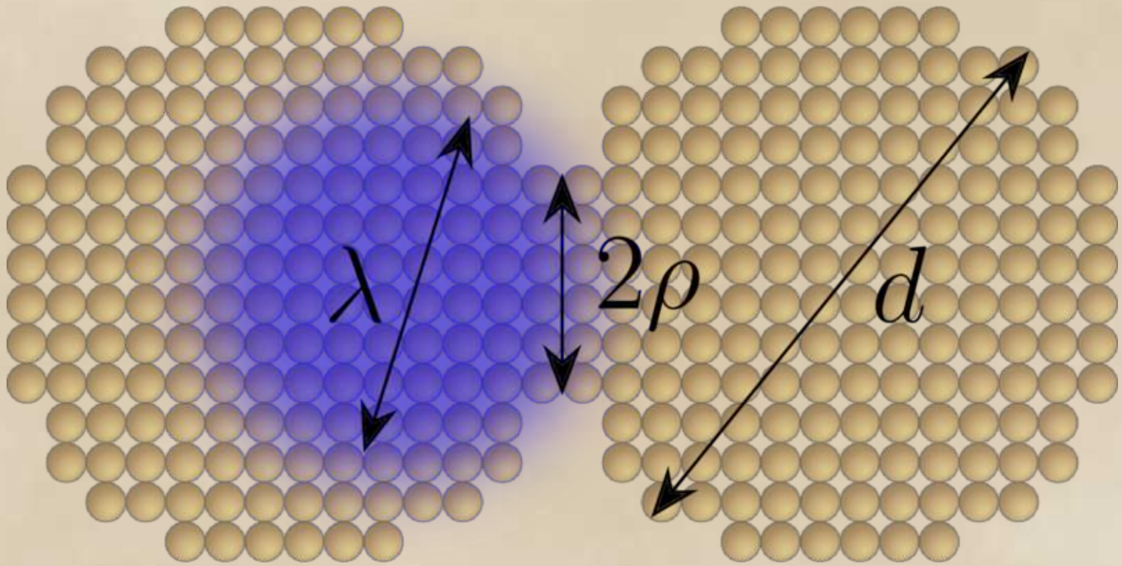
$$n_c \simeq \frac{1}{\rho^3}$$



Nature Materials (2016)

Approaching metal-insulator transition from insulator side

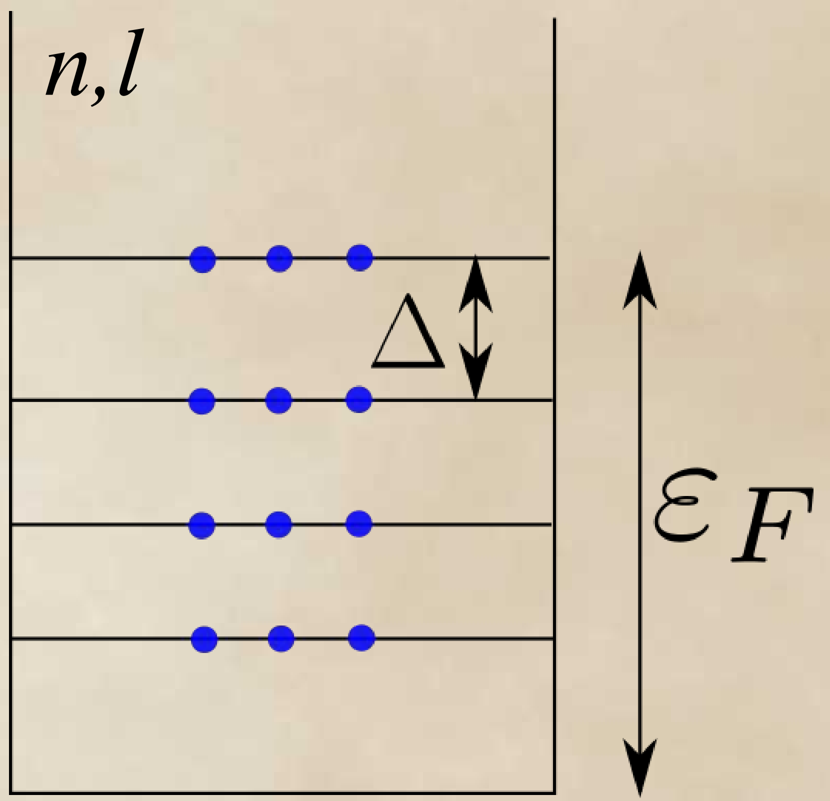
$$n_M \ll n \ll n_c$$



$$\rho \ll \lambda$$

Energy spectrum

(2*l*+1)-degenerate levels



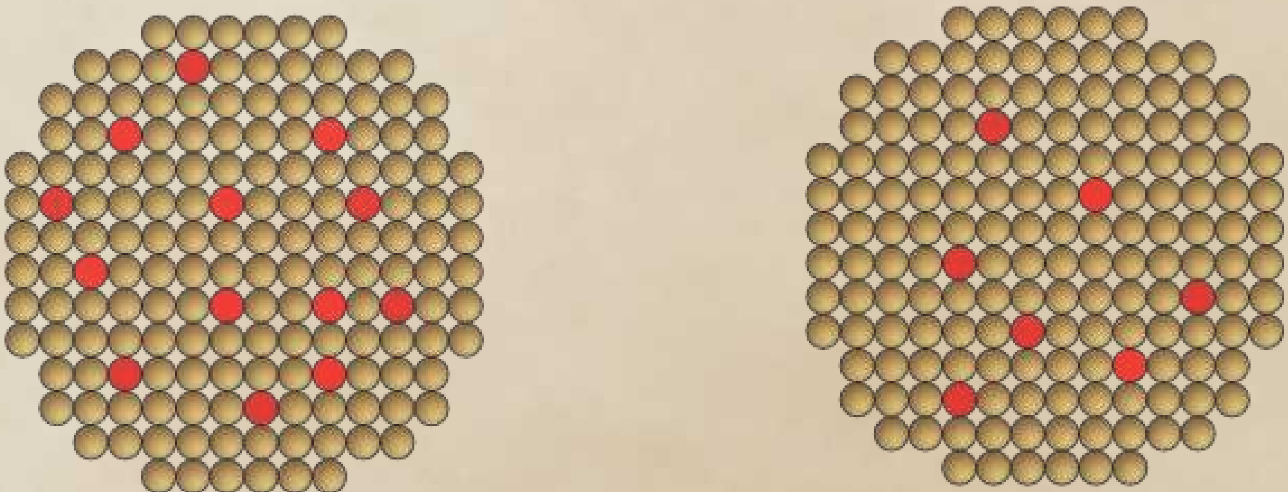
$$\Delta = \frac{\hbar^2}{md^2}$$

$$N = nd^3$$

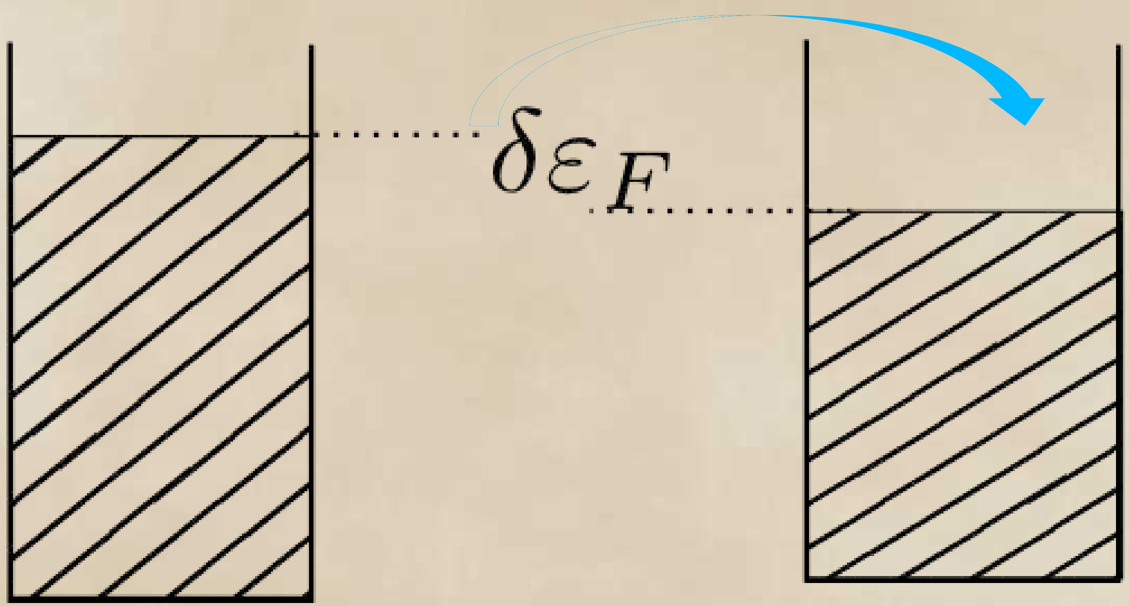
$$\varepsilon_F = \frac{\hbar^2}{md^2} N^{2/3} = N^{2/3}\Delta$$

$$\varepsilon_F = \frac{\hbar^2}{m\lambda^2}$$

Neutral nanocrystals with different numbers of donors

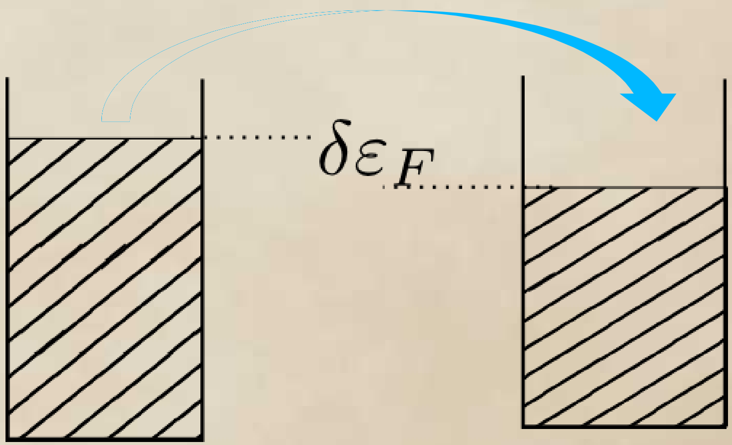


$N + \sqrt{N}$ $\qquad\qquad$ $N - \sqrt{N}$

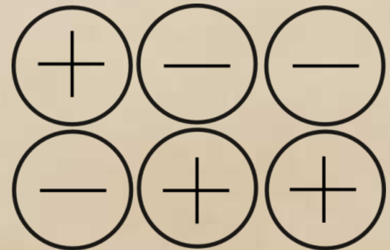


$$\delta\varepsilon_F = N^{1/6}\Delta$$

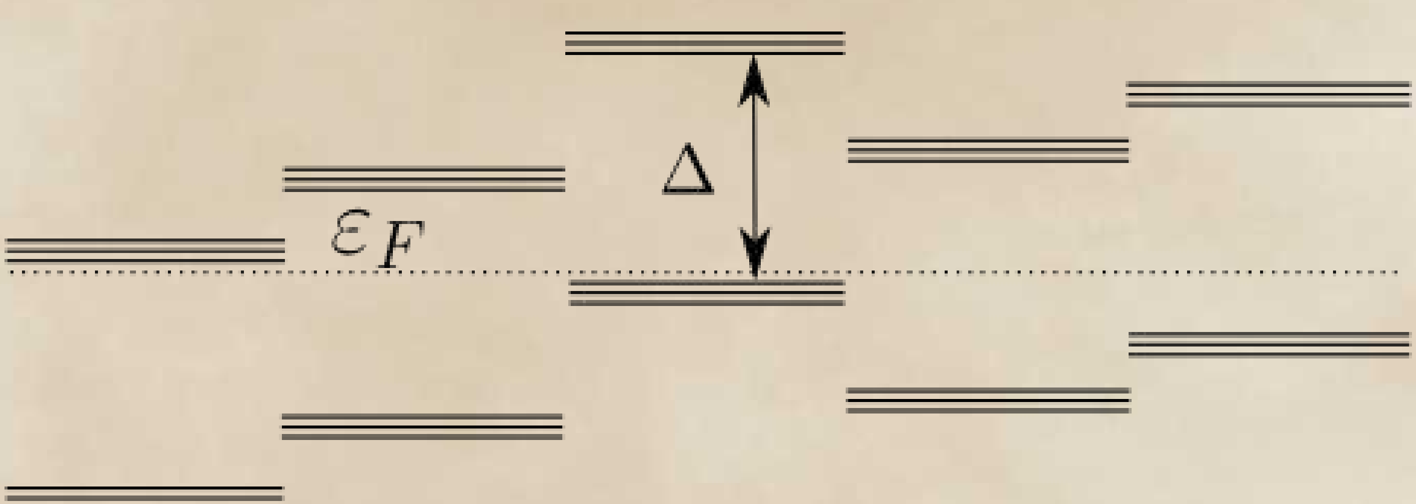
Charging of nanocrystals



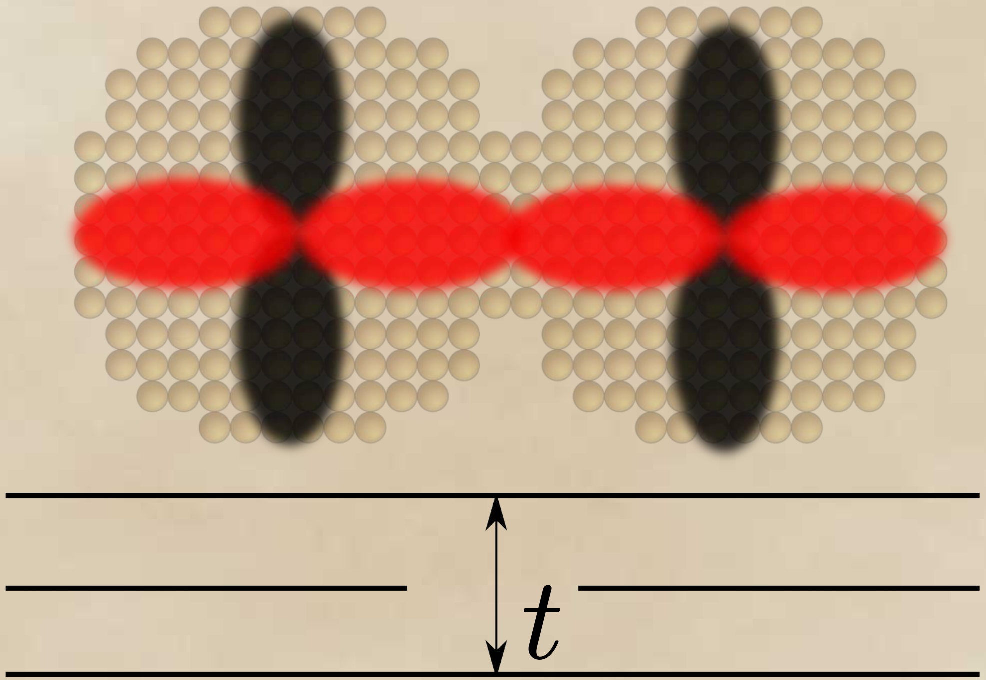
$$Q \sim \sqrt{N}$$



+ Diameter variations



Wave functions of electrons inside a nanocrystal

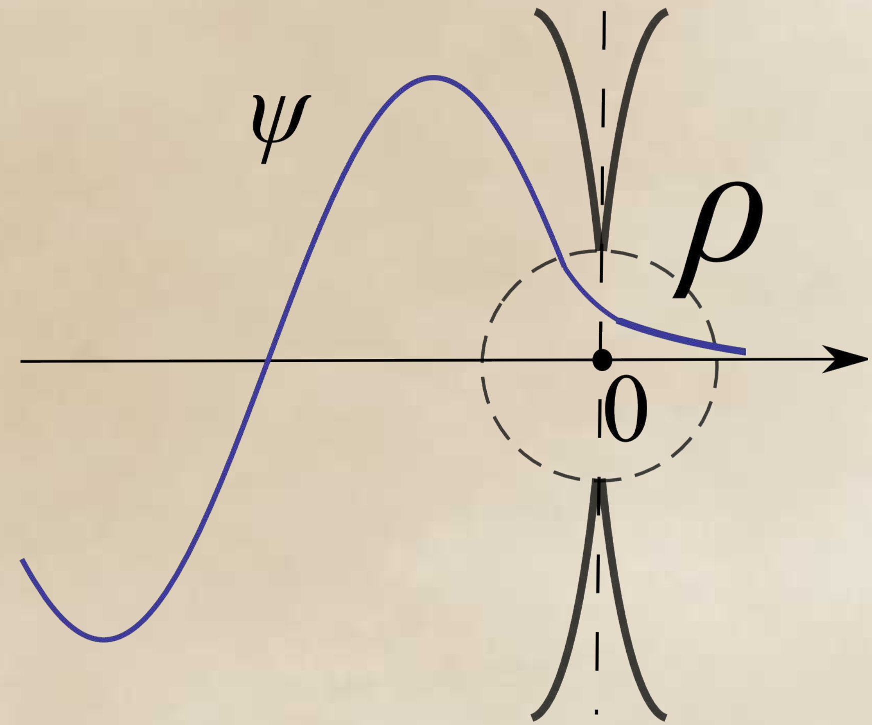


$$t \simeq \frac{\hbar}{\tau} \simeq \hbar \int j dS \simeq \frac{\hbar^2}{m} \int \frac{d\psi}{dx} \psi dS$$

Evaluation of t

$$\frac{d\Psi}{dx} \simeq \frac{1}{\lambda^{3/2} d}$$

$$\Psi \simeq \frac{\rho}{\lambda^{3/2} d}$$

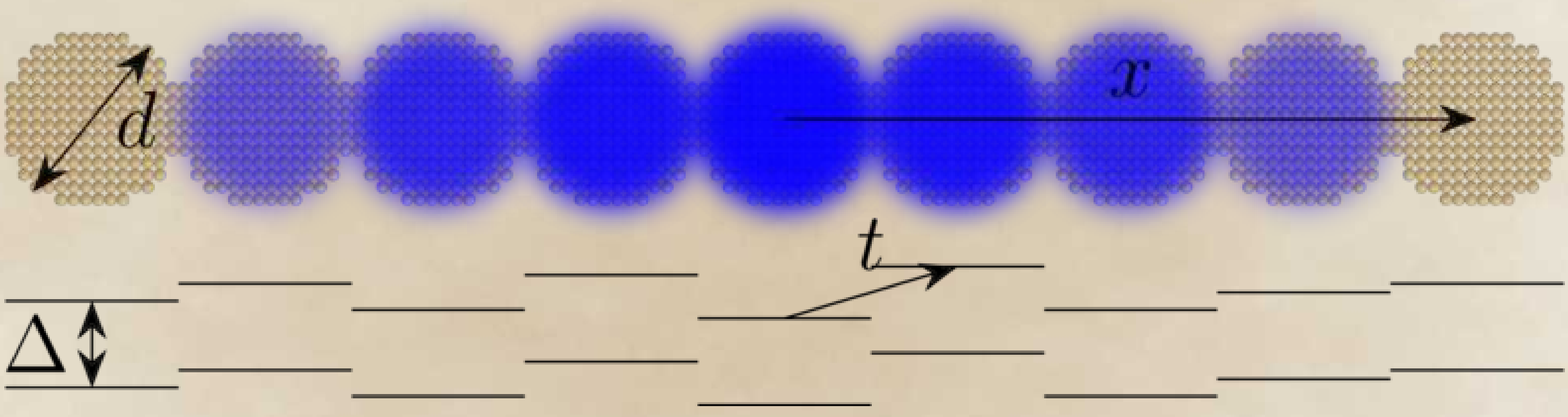


$$t = \frac{\hbar^2}{m} \int \frac{d\Psi}{dx} \Psi dS = \frac{\hbar^2}{md^2} \left(\frac{\rho}{\lambda}\right)^3$$

PRB (2016)

Calculating localization length

$$\Psi \sim \exp\left(-x/\xi\right)$$

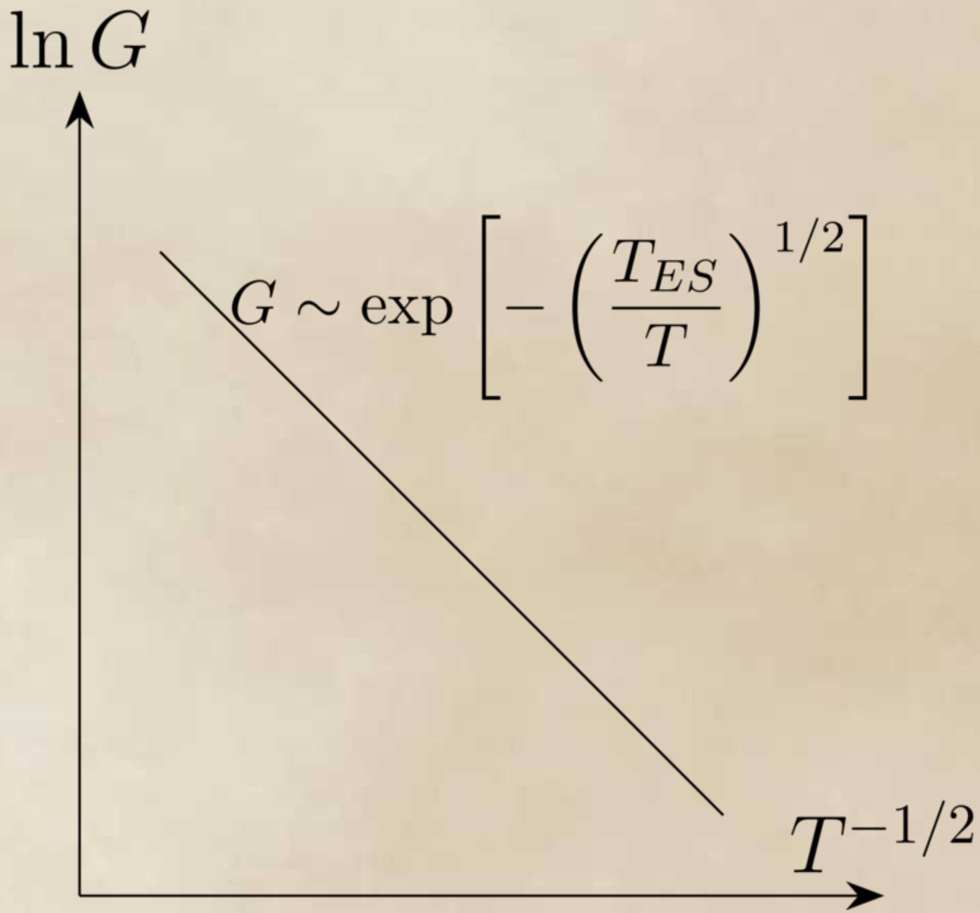


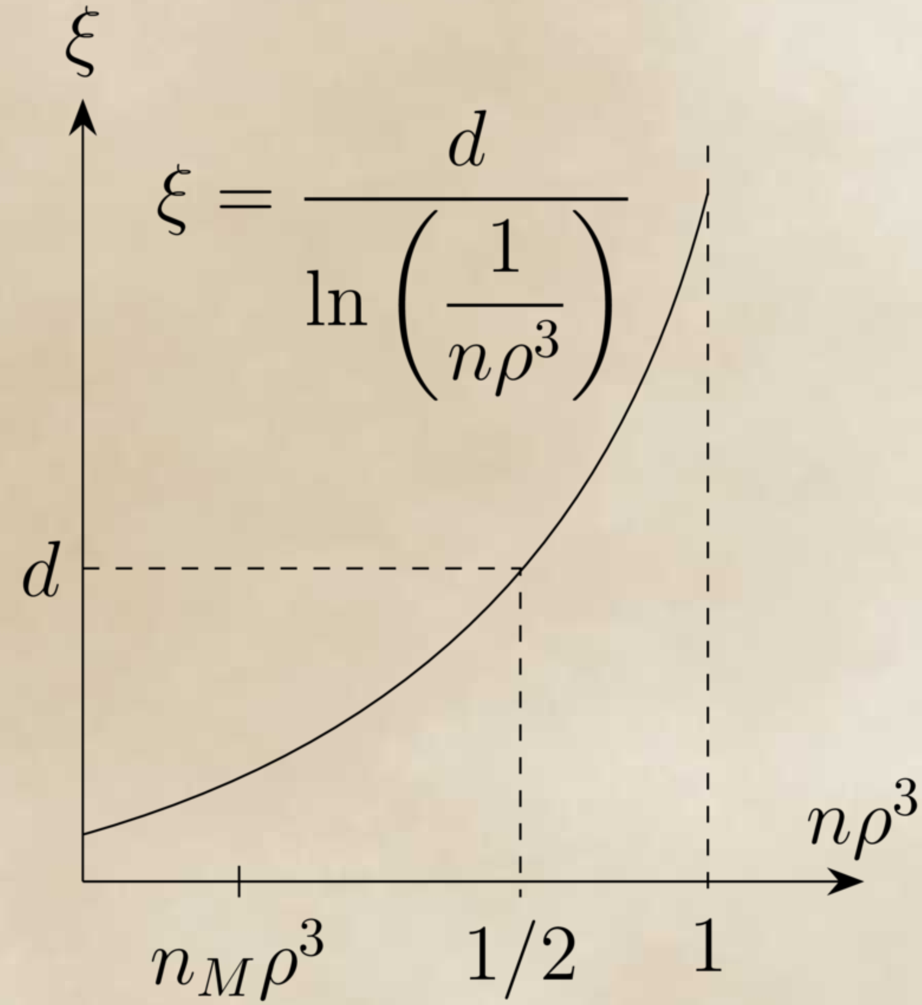
$$\left(\frac{t}{\Delta}\right)^{x/d} \propto \exp\left(-\frac{x}{\xi}\right) \qquad \xi \simeq \frac{d}{\ln(\Delta/t)}$$

Transition happens at $\Delta = t$

$$\rho \simeq \lambda \simeq n_c^{-1/3}$$

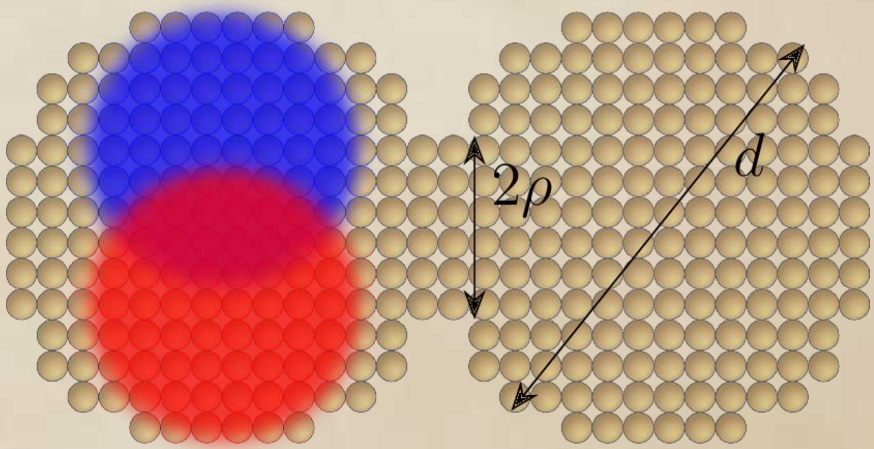
Metal-insulator transition from insulator side

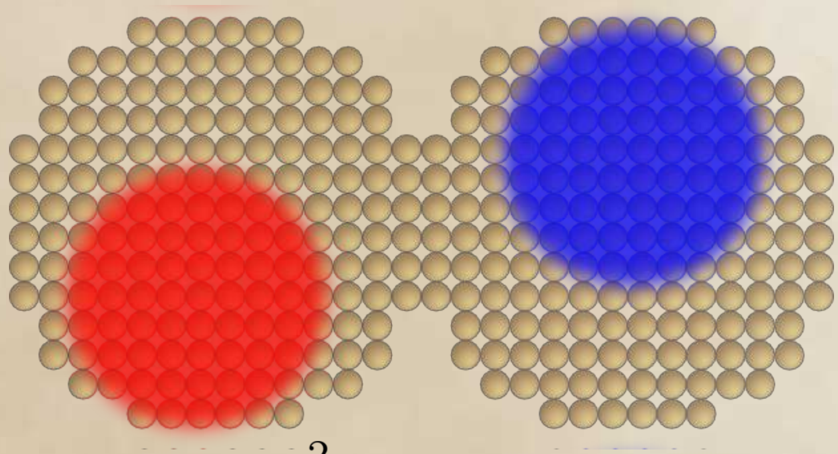




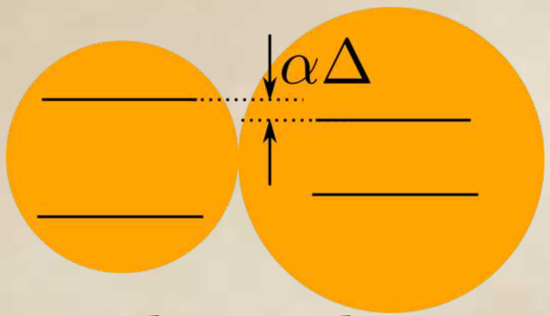
$$T_{ES} \sim \frac{e^2}{\xi(n)}$$

Exciton hopping between nanocrystals





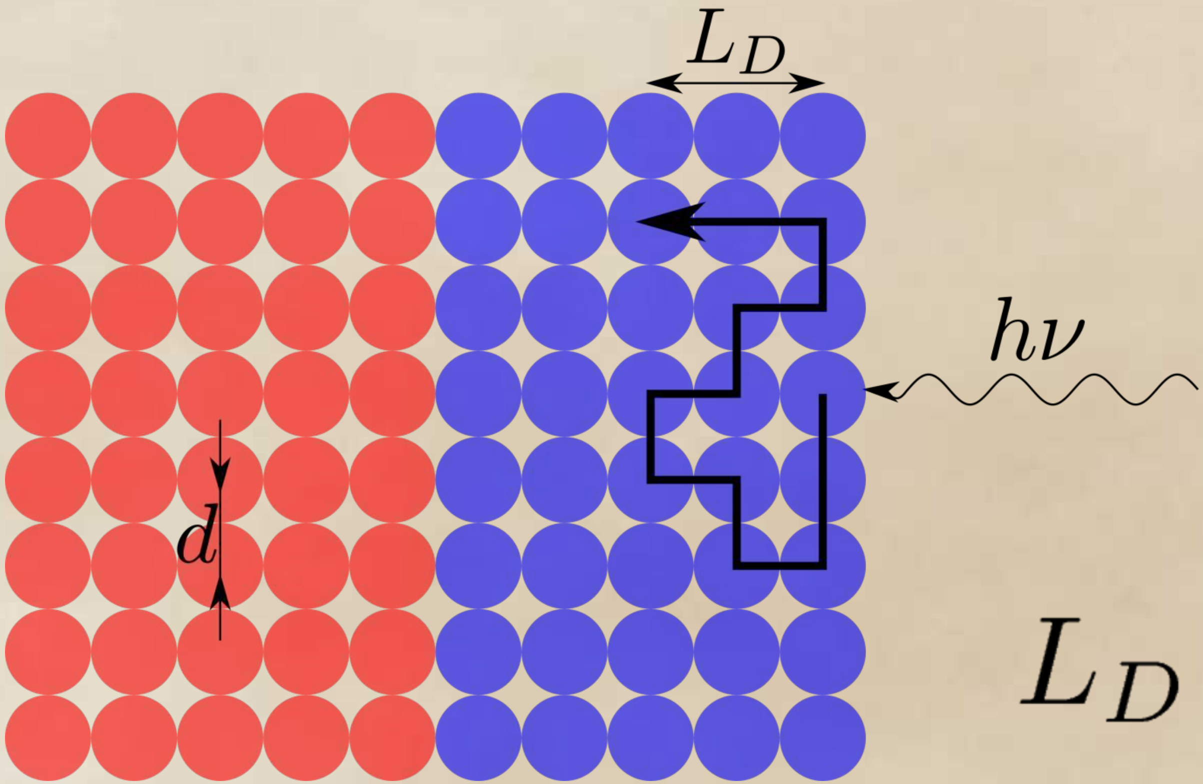
$$E_c = \frac{e^2}{\kappa d} \qquad E_c \gg T$$



$d \pm \alpha d$

$$t \ll \alpha\Delta \ll E_c \ll \Delta$$

p-n junction solar cell

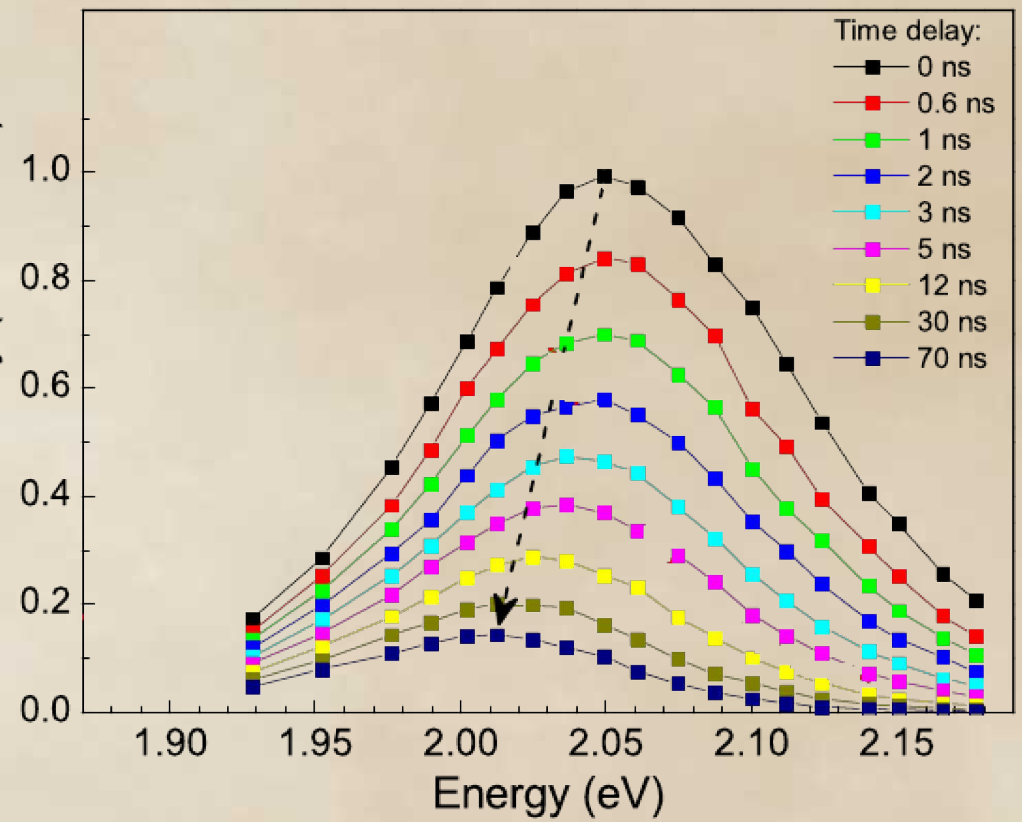


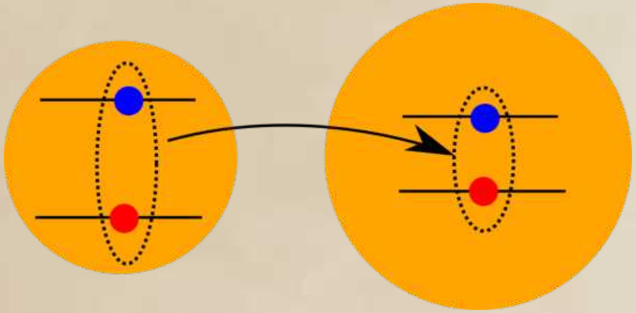
$$L_D \sim \sqrt{\frac{\tau_l}{\tau_h}} d$$

τ_l-life time

τ_h-hopping time

Experimental study: photoluminescence

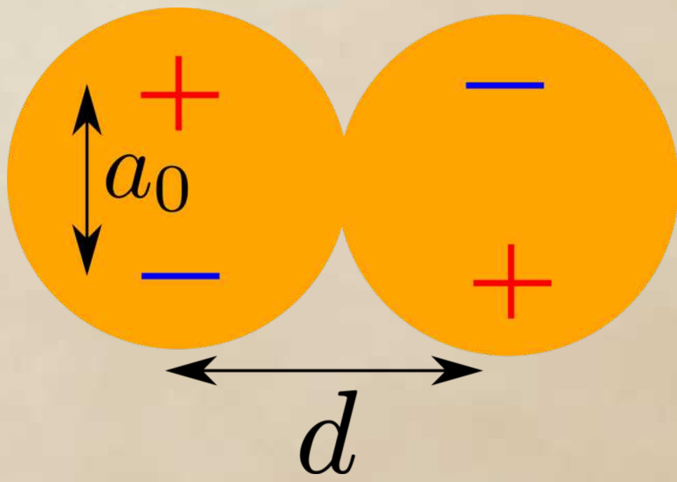




$$\frac{1}{\tau_h} \sim |M|^2$$

Bayer et all, PRB (2015)

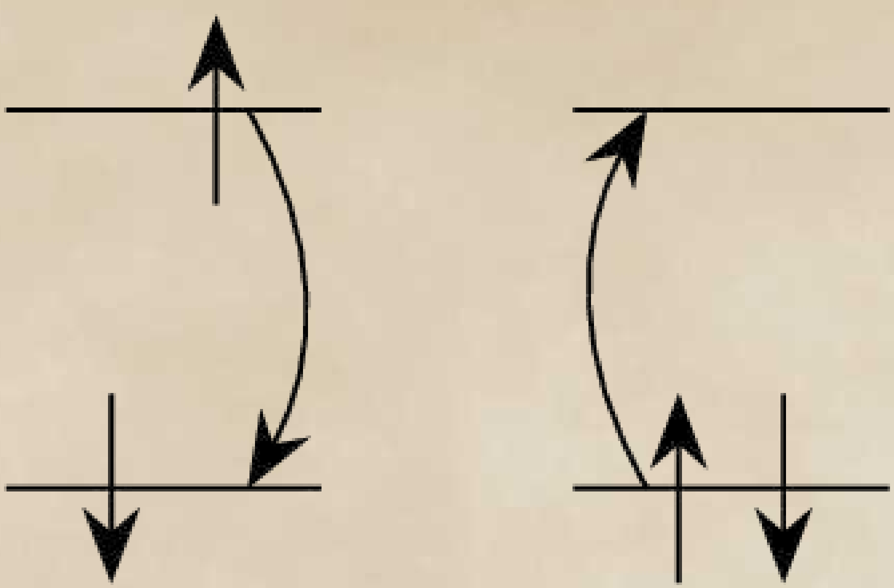
Forster transfer



$$M_F = \frac{e^2 a_0^2}{\kappa d^3}$$

PbSe

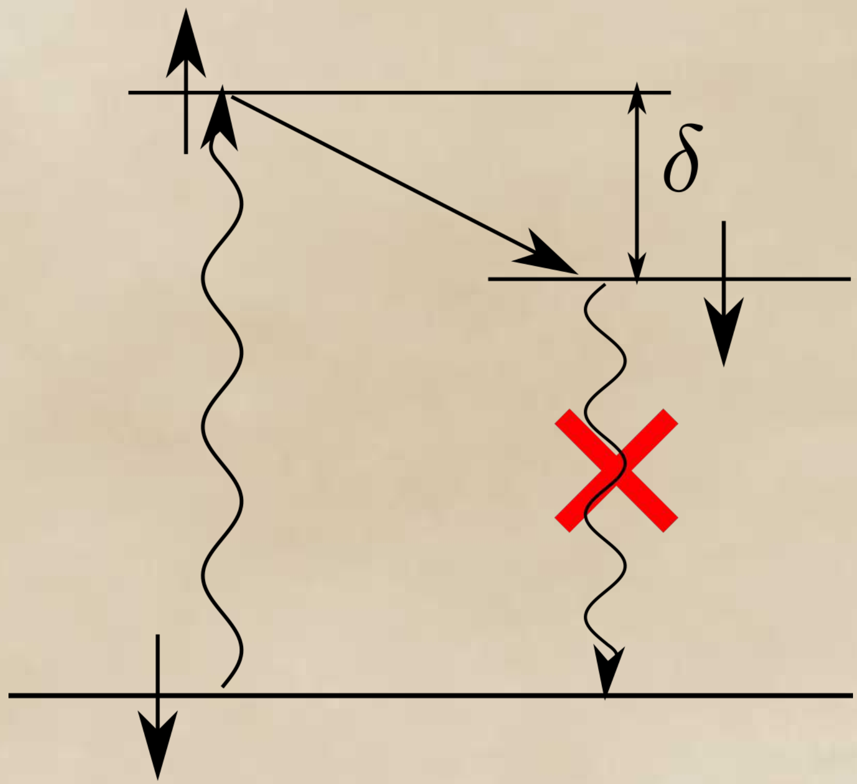
orbitals Pb



orbitals Se

$$a_0 \simeq a$$

Forster troubles in direct semiconductors like PbSe

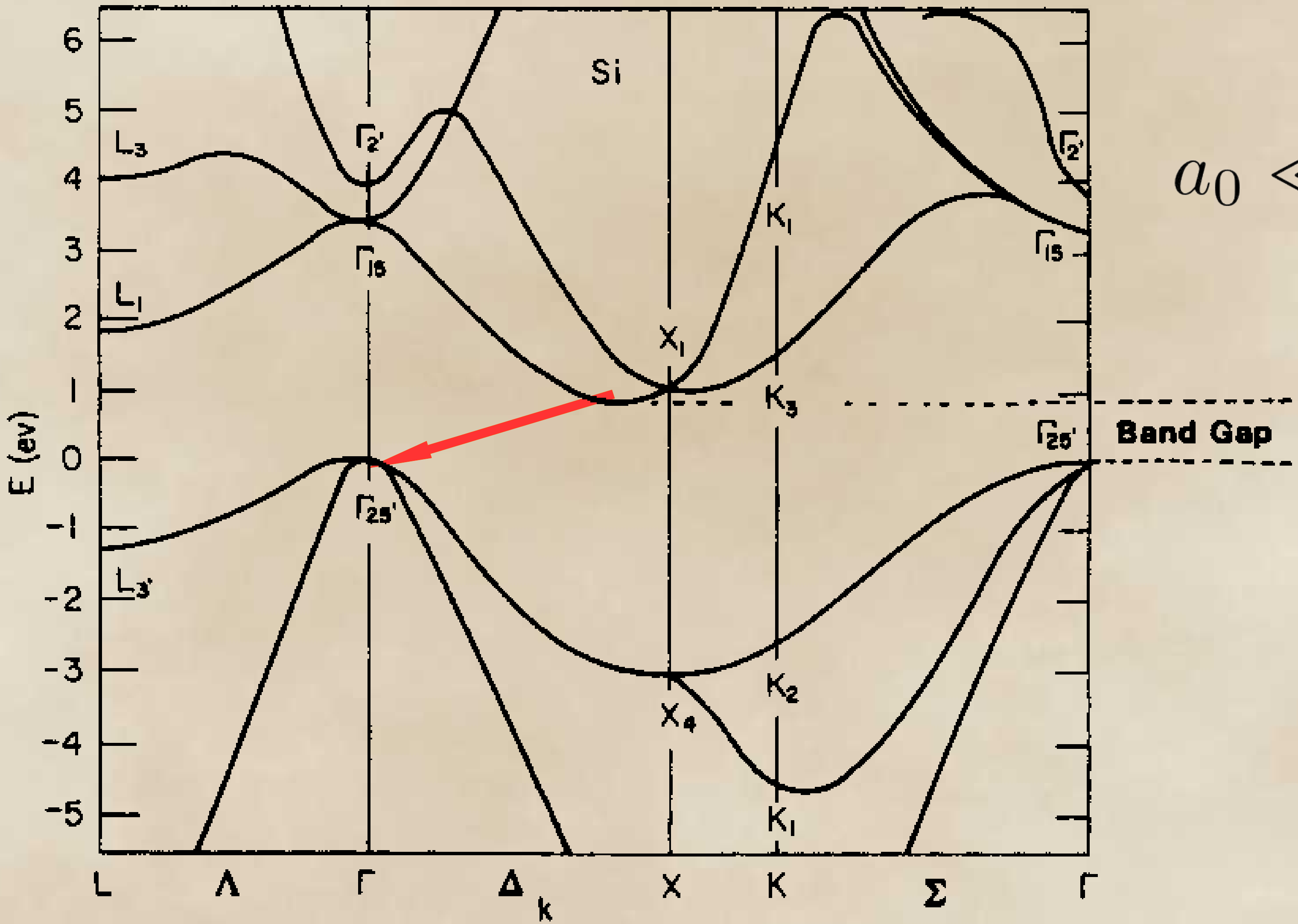


$$a_0 \ll a$$

$$\delta = \int \Psi_S^*(r_1, r_2) \frac{e^2}{|r_1 - r_2|} \Psi_S(r_1, r_2) d^3 r_1 d^3 r_2$$

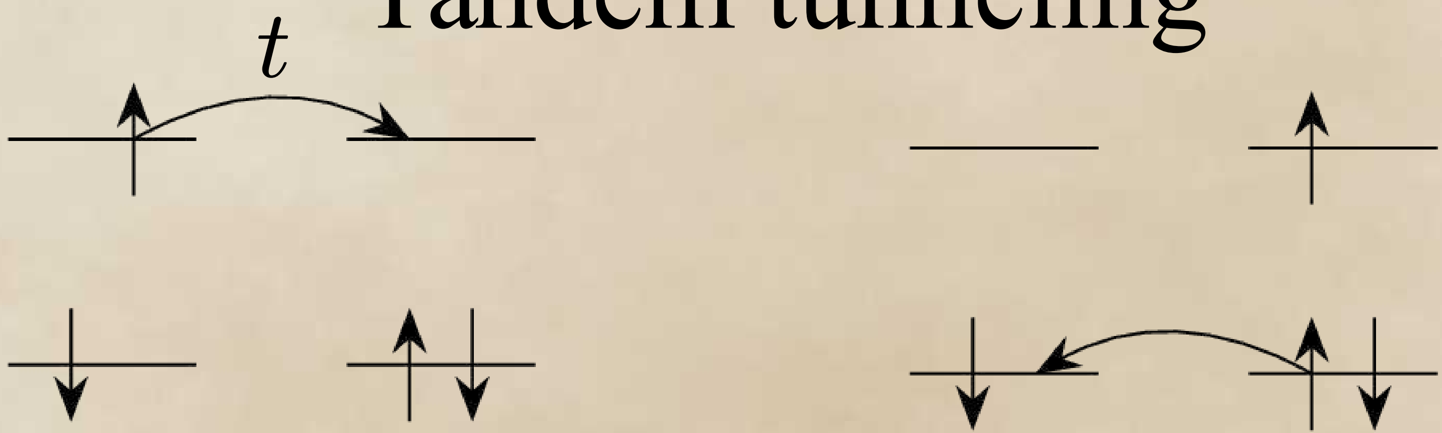
$$\Psi_T(r_1 = r_2) = 0$$

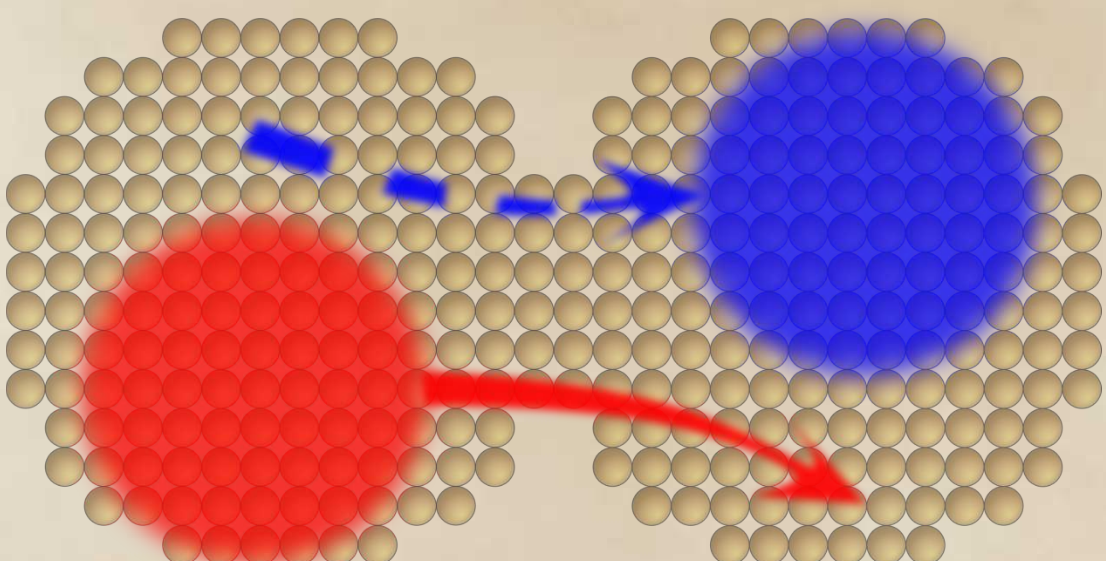
Forster troubles in Si and other indirect semiconductors:Forbidden dipole transition



$$a_0 \ll a$$

Forster alternative: Tandem tunneling





$$M_T = \frac{t^2}{E_c}$$

ACS Nano (2016)

Room temperature comparison

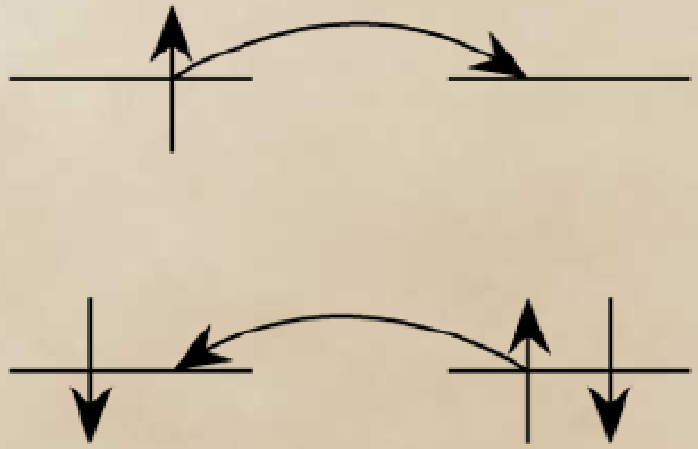
$$M_T = \frac{t^2}{E_c}$$

$$M_F = \frac{e^2 a_0^2}{\kappa d^3}$$

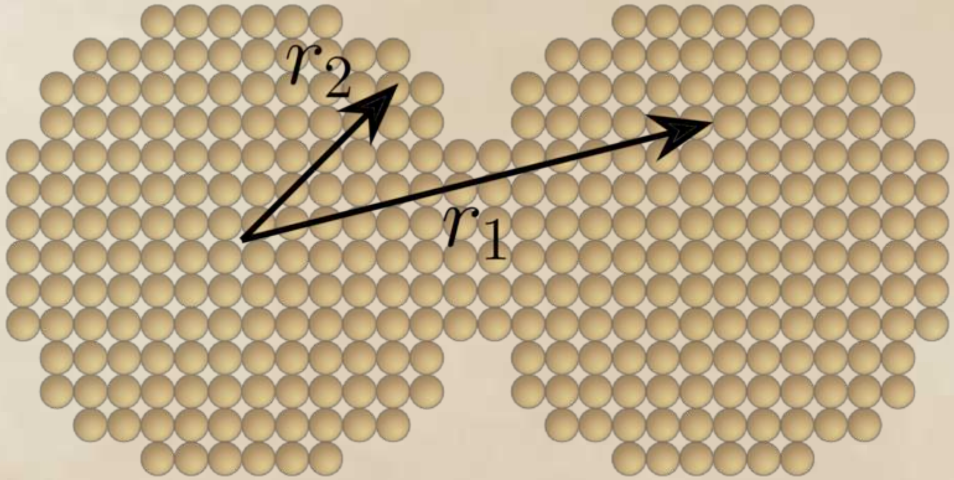
NC	τ_T^{-1}/τ_F^{-1}
InP	0.2
CdSe	0.1
ZnO	10^{-2}
Si	10^3
PbSe	0.1

$$\frac{\tau_T^{-1}}{\tau_F^{-1}} = \left(\frac{M_T}{M_F}\right)^2 = \left[\frac{\Delta}{E_c}\frac{d}{a_0}\left(\frac{\rho}{d}\right)^3\right]^4$$

Dexter transfer



$$M_D = \int \Psi^{L*}(r_1)\Psi^{R*}(r_2)V(r_1,r_2)\Psi^R(r_1)\Psi^L(r_2)d^3r_1 d^3r_2.$$



$$V(r_1, r_2) = 0$$

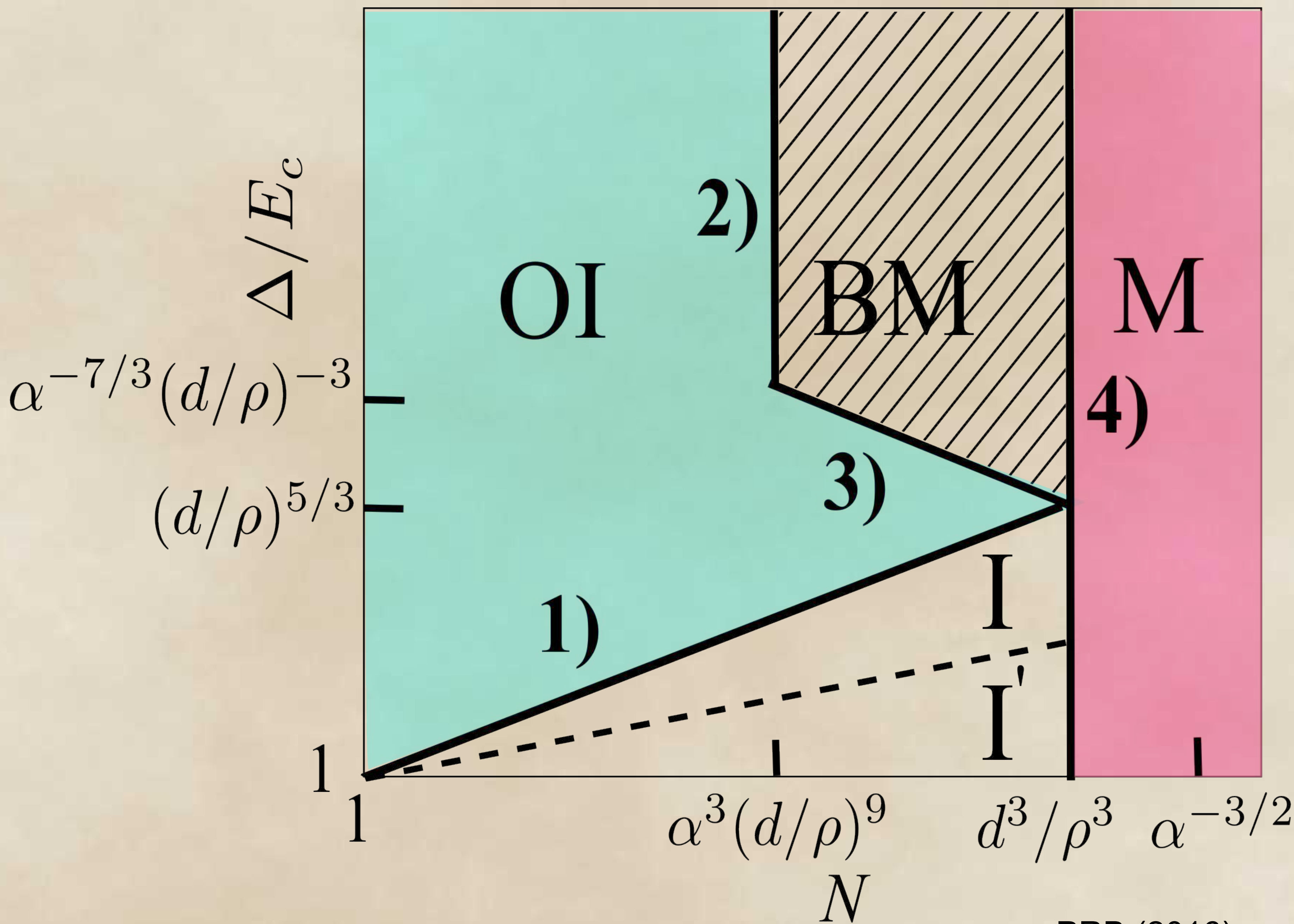
$$V(r_1, r_2) = E_c$$

Comparison

$$M_T = \frac{t^2}{E_c}$$

$$M_D = E_c \left(\frac{t}{\Delta}\right)^2$$

$$\frac{\tau_T^{-1}}{\tau_D^{-1}} = \left(\frac{M_T}{M_D}\right)^2 = \left(\frac{\Delta}{E_c}\right)^4 \gg 1$$


Δ/E_c
$\alpha^{-7/3}(d/\rho)^{-3}$
$(d/\rho)^{5/3}$
1
OI
BM
M
2)
3)
4)
1)
I
I'
1
$\alpha^3(d/\rho)^9$
d^3/ρ^3
$\alpha^{-3/2}$
N

PRB (2016)